

Reseña Tesis. Alternative anodic materials for the development of sustainable lithium-ion batteries.

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OBJETIVES AND NOVELTY

Lithium-ion batteries (LIBs) are the most attractive and feasible alternative for the development of massive electrical energy storage systems to allow the implementation of renewable energy sources as well as the electric vehicle, thus contributing to the transition from an energy model based on fossil fuels to other more sustainable. Nevertheless, it is necessary to identify new environmentally friendly electrode materials (active materials, binders) capable of improving the LIBs performance without increasing the cost. Therefore, the Main Objective of this Thesis is to develop efficient anodes for LIBs to improve the energy and power of these devices as well as the battery life, reducing the environmental impact associated with their manufacture, use and subsequent recycling. To achieve this goal, the work is organized in three activities that are related to the following Specific Objectives:

- To prepare graphitic nanomaterials from biogas-derived carbon nanofibers with suitable structural, textural and electrical properties to be used as anodes in LIBs. The carbon nanofibers are produced by catalytic decomposition of biogas, a renewable energy source which has been exploited to this end for the first time.
- To substitute the fluorinated organic compounds, the binders in the anodes of LIBs, by natural bio-derived, water-soluble, harmful and biodegradable polymers known as hydrocolloids. These environmentally friendly biopolymers are basically employed in the food and pharmaceutical industrial sectors, therefore, the proposed application is absolutely innovative, and would also allow the opening of new markets for these products in the field of energy.
- To prepare silicon/biogas-derived carbon nanofibers *composite* materials, through an easily scalable procedure, to be further used as anodes for high-power lithium-ion batteries.

RESULTS

In a first activity, graphitic nanomaterials (graphite nanofibers) with a highly-developed tri-dimensional structure and low porosity (**Table 1**) were achieved by heat treatment at high temperatures of carbon nanofibers produced in the catalytic decomposition of biogas.

Specifically, more structurally ordered materials were obtained from carbon nanofibers by adding silica because of the catalytic effect of the silicon in the presence of the inherent nickel and cobalt

metals. Furthermore, it appeared that the fishbone microstructure facilitates the graphitization of the carbon nanofibers. The graphite nanofibers were further tested as anode active material for lithium-ion batteries. Provided comparable development of the crystalline structure, particularly the crystal thickness (a key factor as regards lithium intercalation), the electrochemical performance of these nanomaterials, in terms of specific capacity ($\sim 250 \text{ mAh g}^{-1}$, after 50 cycles at 37.2 mA g^{-1}), capacity retention (70-80 %) and cycling efficiency (100%), is comparable, or even superior at high-density currents (**Fig. 1**), to that of oil-derived micrometric graphite, which is used on a large scale for LIBs. Therefore, this result can be associated with the nanometric particle size as well as the larger surface area of the graphite nanofibers which, respectively, reduces the diffusion time of the lithium ions for the intercalation/de-intercalation processes, allowing faster charge/discharge rates, and increases the contact area at the anode active material/electrolyte interface which may improve the lithium ions access, i. e. charge transfer reaction. By contrast, the larger surface area of the graphite nanofibers leads to higher irreversible consumption of lithium ions during the SEI formation.

Table 1. Interlayer distance d_{002} , crystallite sizes L_c and L_a , and surface area S_{BET} of graphite nanofibers (BCNF) and reference graphite (SG).

Material	d_{002} (nm)	L_c (nm)	L_a (nm)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
BCNF167/28	0.3362	35.4	99.6	21
BCNF177/28	0.3360	46.8	>100	33
BCNF267/28	0.3370	21.6	55.9	37
BCNF277/28	0.3364	31.1	62.9	45
BCNF27*7/28	0.3363	48.3	>100	36
SG	0.3360	47.0	99.5	5

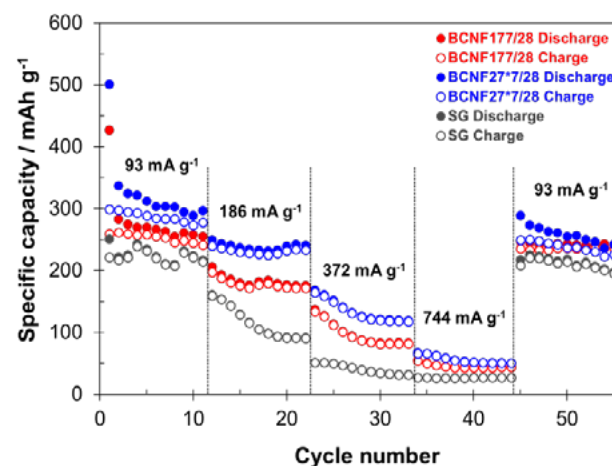


Fig. 1. Cycling performance of graphite nanofibers and reference graphite at different electrical current densities.

Afterwards, a series of hydrocolloids were investigated as potential alternative binders to replace the polyvinylidene difluoride (PVDF), a synthetic fluorinated polymer, used in the graphite anodes of the commercial LIBs, namely agar-agar (AA), carrageenan (CAR) and guar gum (GG) which have not been investigated for this application previously, sodium carboxymethyl cellulose (Na-CMC), sodium alginate (Na-ALG), xanthan gum (GX) and gum arabic (GA). All of them proved to be thermally and electrochemically stable in the range of temperatures and potentials in which these batteries operate as assessed by thermogravimetric analysis cyclic voltammetry, respectively. Focusing on hydrocolloid concentration and nature, the electrochemical response of graphite electrodes containing those of linear structure (Na-Alg, Na-CMC, GG, GX) at 5 wt% was comparable or slightly superior to that of electrodes with 8 wt% of PVDF as binder. Capacities up to 300 mAh g⁻¹ and capacity retentions of 100 % were measured for graphite anodes using these hydrocolloids at electrical current density of 37.2 mA g⁻¹. Furthermore, they showed good rate performance on increasing electrical current density, particularly from 37.2 mA g⁻¹ to 186 mA g⁻¹, providing up to 190 mAh g⁻¹ at the last one which is comparable to that of PVDF-based graphite electrode (Fig. 2).

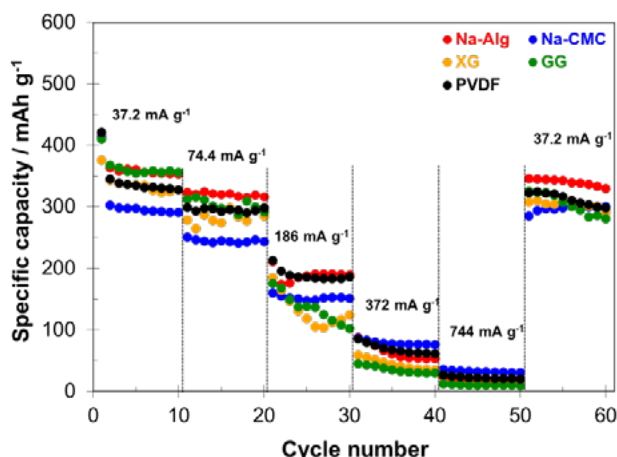


Fig. 2. Cycling performance at variable electrical current density of graphite electrodes with 5 wt% of Na-CMC, Na-ALG, XG and GG, or 8 wt% of PVDF.

Finally, silicon/carbon nanofibers composites were prepared by different methods and they were used as active mixtures in the electrodes, taking advantage of the theoretical capacity of silicon, which is 10 times higher than that of graphite, and the capability of the nanofibers to act as a matrix to accommodate the volume changes associated with the lithiation/de-lithiation process in silicon, that causes a progressive degradation of the electrode. Once the electrode preparation was optimized in terms of type and ratio of the different components (Si/C active mixture, binder, conductive additive), as well as the potential window applied during cycling, it can be concluded that the most suitable electrodes are those with an active mixture made up of nanosilicon/biogas-derived carbon nanofilaments with a certain surface area and porosity, Na-CMC as a binder and carbon black as a conductive additive. Thus, specific capacities up

to 2.5 times higher than the graphite electrode were registered, with comparable capacity retentions and efficiencies, or even up to 5 times higher at elevated density currents (Fig. 3), which implies an outstanding increment of the energy and power densities of the battery.

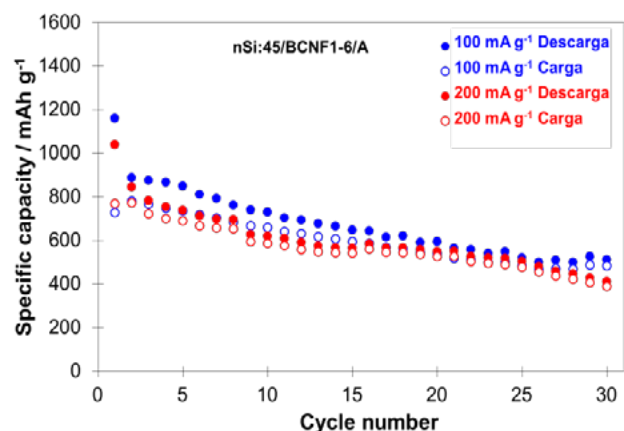


Fig. 3. Cycling performance of Si/carbon nanofiber composite electrode at 100 mA g⁻¹ and 200 mA g⁻¹.

CONCLUSIONS

The development of this work has allowed to identify a series of alternative active materials and binders for their use in the anodes of LIBs that improve the performance and, at the same time, reduce the environmental impact caused by these devices, thus contributing to the definitive implementation of the electric vehicle and the massive electrical energy storage systems in a sustainable way. The main conclusions drawn are detailed below:

- The preparation of graphite nanofibers by high-temperature heat treatment of biogas-derived carbon nanofibers and their subsequent use as active material in the anodes of LIBs is feasible. The electrochemical performance as anodes of these nanofibers is comparable (at low current densities) and even higher (at high current densities) to the micrometric oil-derived graphite that is massively used for this purpose in commercial LIBs.
- The use of the Na-CMC, Na-ALG, XG and GG hydrocolloids (the latter, never before considered for this purpose) as binders in graphite anodes of LIBs as a substitute of PVDF, is absolutely viable. Taking into account also the price and the possibility of using water instead of an organic solvent, the implementation of these hydrocolloids in commercial LIBs would mean a significant reduction of costs as well as the environmental impact associated with these devices.
- The use of biogas-derived carbon nanofibers as matrix and Na-CMC hydrocolloid as binder substantially improves the capacity retention of the silicon-based anodes, allowing to accommodate more easily the changes of volume that causes the lithiation/de-lithiation process in its structure. Moreover, all this has been possible through an easily scalable preparation process for the Si/C composites.

RELATED PUBLICATIONS

^[1] de Llobet S, Pinilla JL, Moliner R, Suelves I, Arroyo J, Moreno F, Muñoz M, Monné C, Cameán I, Ramos A, Cuesta N, García AB. Catalytic decomposition of biogas to produce hydrogen rich fuel for SI engines and valuable nanocarbons. *Int J Hydrogen Energy* 2013; 38:15084-15091.

^[2] Cuesta N, Cameán I, Ramos A, de Llobet S, García AB. Graphitic nanomaterials from biogas-derived carbon nanofibers. *Fuel Process Technol* 2016; 152:1-6.

^[3] Cuesta N, Cameán I, Ramos A, García AB. Graphitized biogas-derived carbon nanofibers as anodes for lithium-ion batteries. *Electrochim Acta* 2016; 222:264-270.

^[4] Cameán I, Cuesta N, de Llobet S, García AB, Moliner R, Pinilla JL, Ramos A, Suelves I. Patente Española P201331057, 2013.

^[5] Cuesta N, Ramos A, Cameán I, Antuña C, García AB. Hydrocolloids as binders for graphite anodes of lithium-ion batteries. *Electrochim Acta* 2015; 155:140-147.

Full Thesis can be downloaded from

<http://hdl.handle.net/10261/143931>